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B. J. Kozioziemski, A. A. Chernov, M. A. Johnson,
J. B. Lugten, E. R. Mapoles, J. W. Pipes, J. D.
Sater

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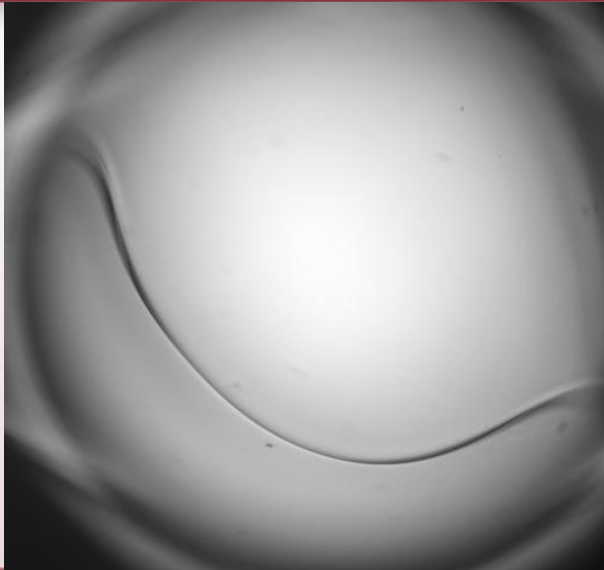
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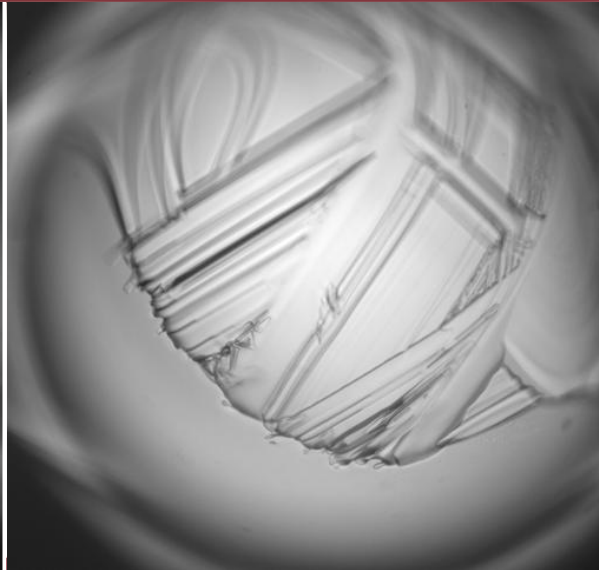
Meta-stable solid hydrogen near the triple-point

B. J. Kozioziemski, A.A. Chernov, M. A. Johnson, J. B. Lugten, E. R. Mapoles, J. W. Pipes, and J.D. Sater

D₂ at 7 hours



D₂ at 7 hours
+ 2 min



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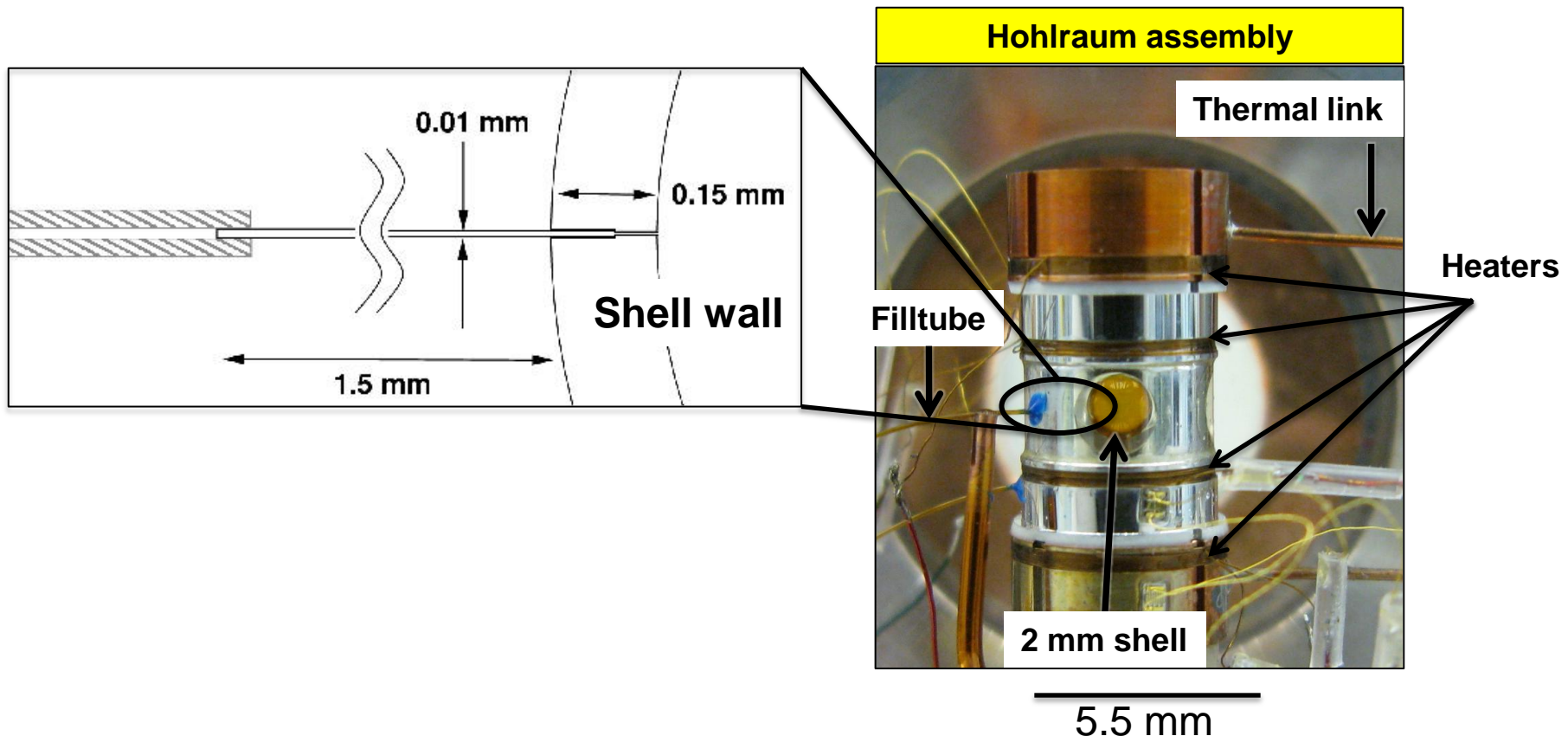
Four observations suggest a meta-stable phase of the hydrogen isotopes at the triple-point

1. Melting temperature of metastable phase is 40 mK, 22.0 mK and 16.5 mK below HCP melting temperature for H₂, D₂ and D-T respectively
 1. Melt temperature difference is $\sim 1/\text{mass}$
 2. Metastable phase converts to the HCP phase, often with multiple grains visible
 3. Metastable phase shrinks once HCP phase nucleates
 4. Growth shape of the metastable phase is isotropic, compared to typically asymmetric growth of HCP phase
- Most seeding attempts produce metastable phase in 5-10 μm borosilcate fill-tubes, rare in 30-40 μm silica fill-tubes

We do not know the structure or origin of the meta-stable phase

The sample is a National Ignition Facility indirect-drive inertial confinement fusion assembly

- 2 mm diameter, 40-150 μm wall plastic or beryllium shell inside of a 5.5 mm dia, 10 mm long cylindrical aluminum hohlraum



We observe two isotope-dependent triple-point temperatures

- $\Delta T_{TP} = T_{TP}^I - T_{TP}^*$, where T_{TP}^I is the phase I (HCP) triple-point temperature, T_{TP}^* is the meta-stable triple-point temperature

Isotope	J = 1	ΔT_{TP} (mK)
H ₂	72-75%	42.0 +- 2.0 mK
H ₂	32-37%	37.5 +- 0.7 mK
D ₂	33%	21.0 +- 1.0 mK
D ₂	12-18%	22.2 +- 0.5 mK
25%D ₂ -50%DT-25%T ₂	< 5%	16.5 +- 1.0 mK
25%D ₂ -50%DT-25%T ₂	2-26%	22.0 +- 1.0 mK

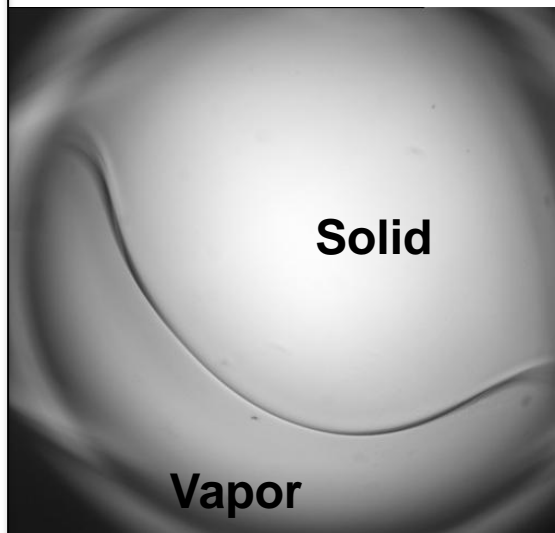
ΔT_{TP} is the best indication we are observing a meta-stable phase

Rapid recrystallization to the HCP phase is observed

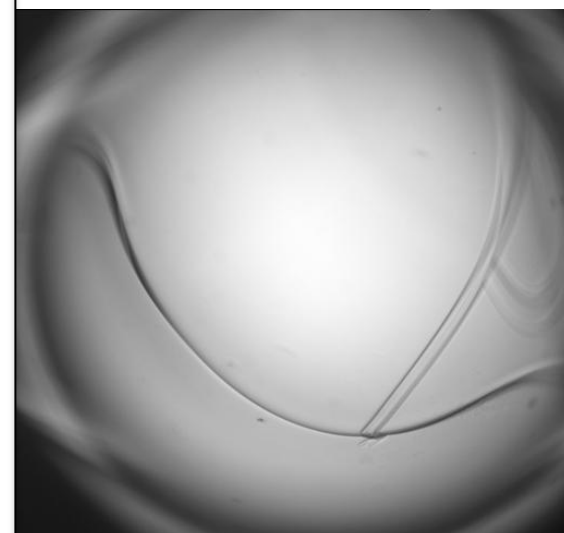
- Example of meta-stable solid D_2 at $T_{TP}^* - 1.5$ mK
- Solidified over ~ 8 hours, solid migrates to top of shell in thermal gradient
- Recrystallization was spontaneous
- D_2 meta-stable solid cooled to $T_{TP}^* - 0.25$ K before recrystallization
- D_2 meta-stable solid persisted ~ 48 hours before recrystallization

2 mm

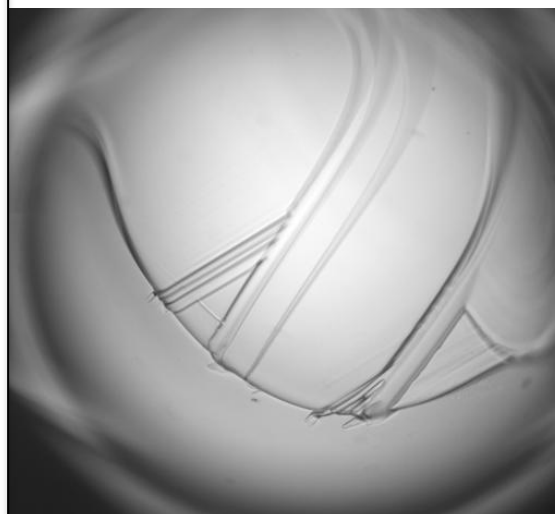
$t = 0$ s, $T = 18.6877$ K



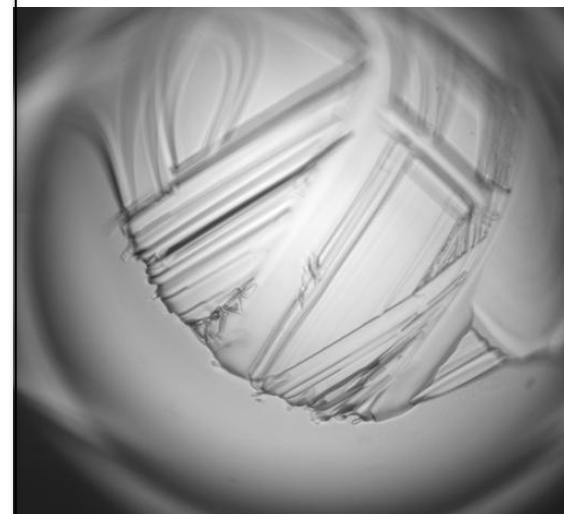
$t = +11$ s, $T = 18.6878$ K



$t = +56$ s, $T = 18.6884$ K

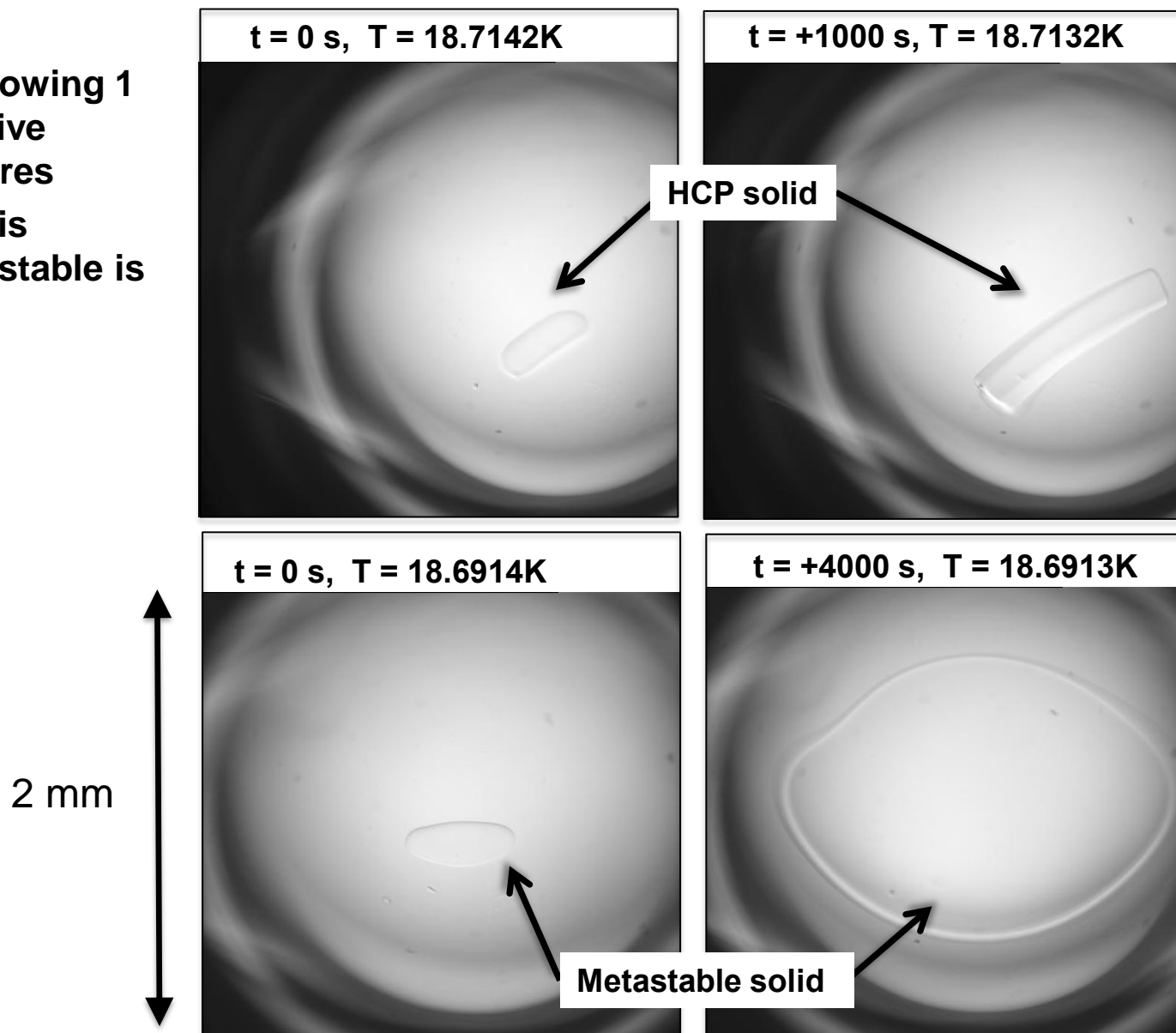


$t = +120$ s, $T = 18.6872$ K



Growth shape of meta-stable solid is isotropic compared to anisotropic hcp growth

- Two D_2 crystals growing 1 mK below respective melting temperatures
- HCP solid growth is anisotropic, meta-stable is isotropic



Two hypothesis for the metastable solid are that it is a real polymorph, or a defect-rich pseudo-phase

- 1) The close-packing requirement may result in fcc, icosohedrons, or even quasi-crystalline structures
 - Ostwald rule of stages states that the less stable polymorph can nucleate first
 - Polymorphs of the rare gas solids near their triple-points have been reported

- 2) Defects in the pseudo-phase increase the chemical potential ($\Delta\mu$) and hence lower the triple-point temperature
 - $\Delta\mu = \Delta T [(s_v - s_s) \{(\omega_L - \omega_s)/(\omega_v - \omega_s)\} - (s_L - s_s)] = 3 \times 10^{-18}$ ergs
 - This is equivalent to strain of $\varepsilon = (2\Delta\mu/E\omega_s)^{1/2} = 6 \times 10^{-3}$
 - ω = molecular volume, s = entropy, E = Young's modulus
 - This amount of thermo-elastic strain was previously observed to generate grain-boundaries, which are not observed in the meta-stable solid

Summary and future plans

- We have observed the hydrogen isotopes to form a meta-stable solid near the triple-point
 - Meta-stable solid has lower melting temperature that is isotope dependent
 - Rapidly recrystallizes to stable phase
 - Growth is isotropic
 - hcp phase consumes the meta-stable phase
- We do not know the origin or nature of the meta-stable solid, but it is likely to be a polymorph
 - We plan x-ray diffraction experiments to determine the solid structure
 - We will test fill-tube modifications to prevent meta-stable solid from forming (for fusion ignition experiments)